

ADVANCED LEAD ACID BATTERY DEVELOPMENT

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EXECUTIVE SUMMARY

The Advanced Lead Acid Battery Development project was funded for a total of \$67,000 over a two-year period. Researchers at the University of Idaho have been investigating the possibility of using lead acid batteries in electric and hybrid vehicles for more than ten years, and the funding from University Transportation Centers Program through NIATT helped support this continuing effort.

The ultimate objective of the funded work was to develop a high performance, long life, lead acid battery for a range-extended hybrid electric vehicle (REHEV). Although we realized that the amount of funding available through UTC was completely inadequate for achieving our objective, we were hopeful that we could use the funds to generate additional outside funding with which we could develop a larger program.

The lead acid battery uses horizontal plates and improved conductor structures to provide high power discharge capabilities (Fig. 1). Our first task was to design a baseline cell to provide 35 w-hr/kg at the two-hour discharge rate, 200 w-hr/kg at 100 percent state of charge (SOC) and 1000 cycles at 80 percent depth of discharge (DOD). This initial design was developed with the expectation of establishing a cell development program with battery manufacturers. The baseline cells, as developed, could serve as the foundation for the future development of advanced cells and eventually, the commercialization of a REHEV.

In the work performed to date, we used conductivity and diffusion computer models previously developed at the University of Idaho, to evaluate the performance of advanced cells having high performance plates. These plates had various conductive and non-conductive additives incorporated into the positive paste to improve the energy performance of the battery. Our models show that, in theory, we should be able to increase the energy performance of the baseline cells from 30-35 w-hr/kg to 60-65w-hr/kg.

Our project also involved improving the conductivity and diffusion models. The improved models were then used to evaluate the occurrence of oxygen evolution in the positive plate so we could understand how the positive active material deteriorates with cycling.

Further development of these models could ultimately be used to understand the failure mechanisms associated with sealed, lead acid batteries and to investigate methods for increasing their life.

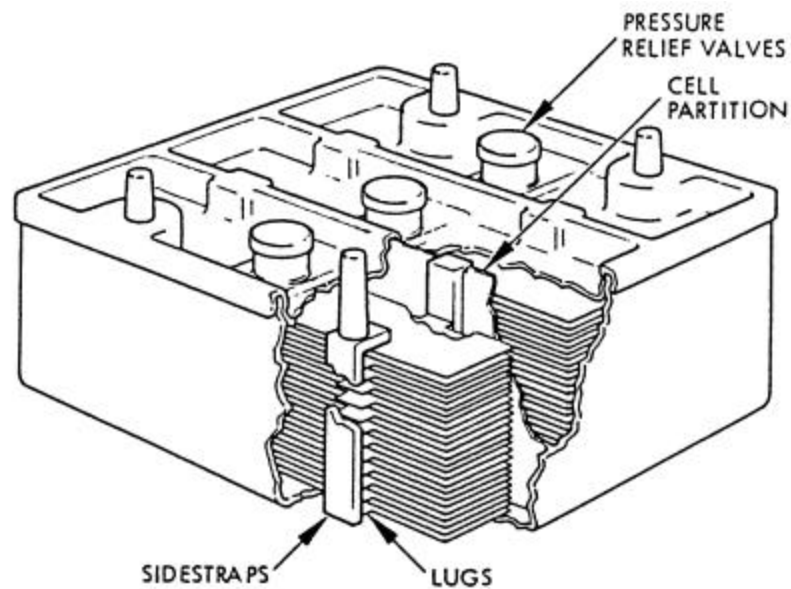


Figure 1. Sealed, lead acid battery using horizontal plate design.

DESCRIPTION OF PROBLEM

A major problem facing the commercialization of hybrid electric vehicles (HEVs) is the battery. Many attempts have been made to develop advanced batteries for HEVs, but all these batteries have suffered from major economic, performance or safety deficiencies. The sealed, lead acid battery is inherently a low cost battery and is the most attractive battery candidate for use in HEVs. However, sealed, lead acid batteries also have performance and life problems that need to be better understood and solved before the commercialization of HEVs can be made possible.

APPROACH AND METHODOLOGY

In an attempt to better understand lead acid batteries and the physical processes that limit their capacity, two computer models were developed to simulate the conductivity of the positive

active material and the diffusion of sulfate ions in lead acid batteries. The conductivity model was developed to estimate the critical volume fraction of paste containing non-conductive or conductive additives [1]. Researchers have found that after a certain amount of the active material in lead acid batteries has reacted, the remaining material becomes isolated and cannot react [2]. The amount of active material that can be discharged before the remaining material becomes isolated is termed the critical volume fraction. Values for the critical volume fraction have been estimated to be approximately 60 percent for homogeneous paste.

In order to model the conductivity of the active material, we assume it is made of spherical particles, which we modeled as nodes on a two-dimensional grid. Each node is connected to the surrounding eight nodes by a conductive pathway. The grid contains over one million nodes (1024 x 1024 nodes). The model randomly chooses a node and attempts to find a conductive pathway to the edge of the grid. If a pathway can be found, the starting node is considered discharged and marked as non-conductive. If a pathway is not found, the starting node is marked as isolated.

After all nodes have been selected and pathways have been tried, the model reports the number of nodes that were either discharged or isolated. The critical volume fraction is calculated as the ratio of discharged nodes to the initial number of available nodes. The model can take into account any non-conductive additives by initially marking those nodes as discharged. For conductive additives, the model marks those nodes as always conductive. The amounts of additives are given as volume percentages, and the size of the individual additive is given relative to the base node size. For example, a non-conductive glass microsphere, approximately 20–50 μm in diameter, is represented as a particle of 10 x 10 nodes. Figure 2 shows the effect on the critical volume fraction of adding conductive and non-conductive additives using this model.

The second model, the diffusion model, uses finite difference equations and Fick's law to estimate the acid concentration in both the negative and positive material as well as between them as a function of time. The Nerst equation is then used to determine the battery potential.

The model combines diffusion and conductivity parameters, including the critical volume fraction from the conductivity model, to estimate lead acid battery performance over a wide

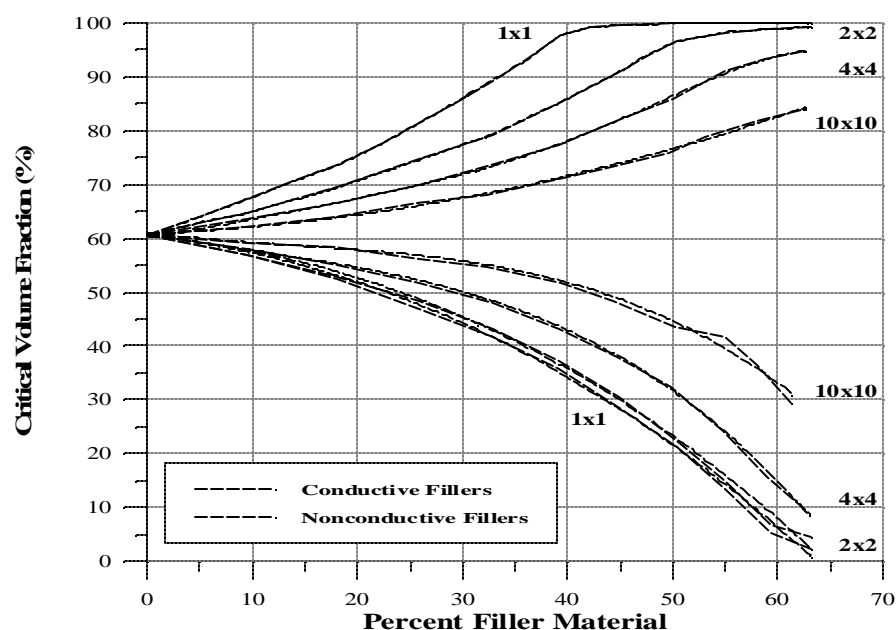


Figure 2. Critical volume fraction with material additives [3].

range of discharge rates. The model produces voltage vs. time curves, percent material reaction curves, and acid concentration plots. Figure 3 shows the amount of material that reacts in both plates at the two-hour rate for the baseline design. The model is helpful in understanding the behavior of lead acid batteries and can be used to develop new cell designs.

Once the plate and cell parameters are established, the model can predict the cell's performance. The model also allows for iterations to determine optimum parameter values. We used these models to examine battery designs that could theoretically double the specific energy performance of lead acid batteries.

In addition to performance problems, the lead acid battery also suffers from some life problems. We used the agglomerate of spheres (AOS) model to examine some life issues. The AOS model was developed over ten years ago [4]. Since that time, the model has been very successful in explaining some peculiar behavior exhibited by lead acid batteries [5–12].

The AOS model views the positive electrode as consisting of spheres connected together through necks. Figure 4 shows two spheres connected by a neck, and this simple figure illustrates the important aspects of the model. The AOS model includes surface tension as one factor affecting the electrode reaction processes. Although the electrode consists of

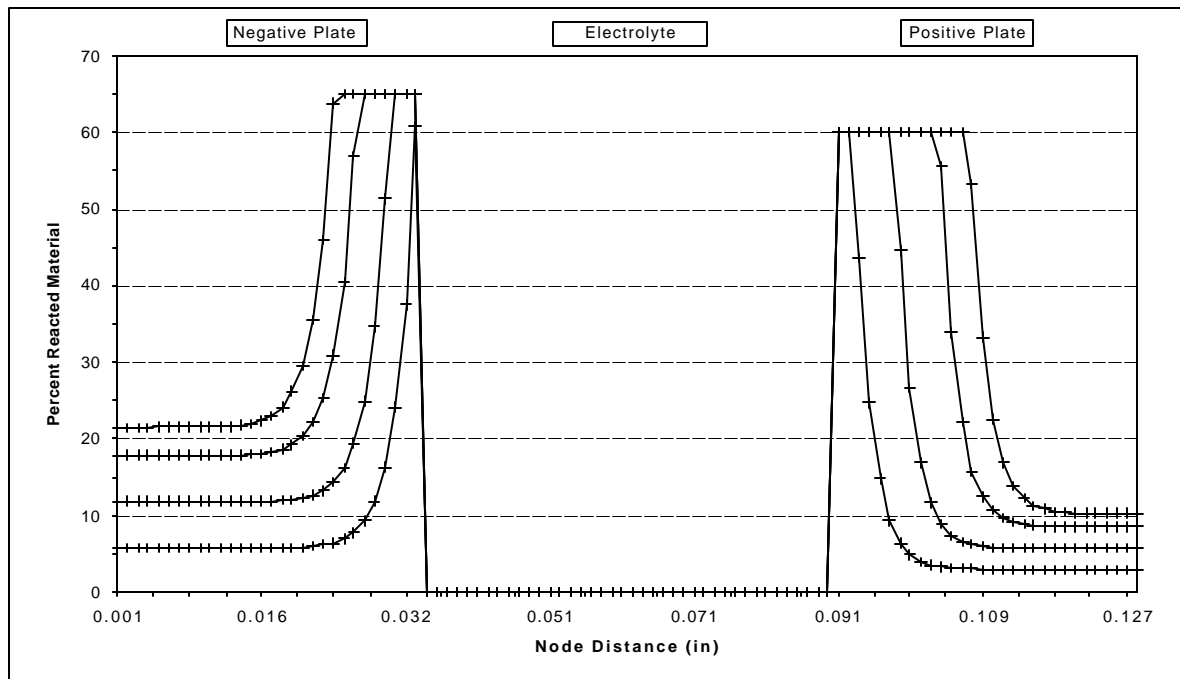


Figure 3. Profiles of reacted material every 2000 seconds of baseline battery at a two-hour discharge rate.

different size particles and necks, the surface of the electrode can still be characterized by different radii of curvatures. The AOS model provides a framework by which these curvatures and the surface tension associated with these curvatures can be analyzed. Our interpretation of the AOS model is that surface tension and the oxygen evolution reaction combine to produce shedding, the usual failure mechanism for deep-cycled lead acid batteries [13].

During our investigations into the AOS model and mechanical compression, we developed an alternative explanation for some features of that model. In this alternative explanation, oxygen evolution in the neck region must be considered along with surface tension when

charging the positive electrode. When the difference in the lattice deficiencies between the neck and sphere produces a potential difference large enough to equalize the potential difference caused by the surface tension between these two regions, then both the neck and

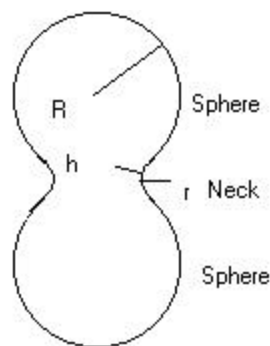


Figure 4. Geometry of AOS model (R =sphere radius; h = neck radius; r = radius of curvature between sphere and neck).

sphere can be charged simultaneously. This requirement reduces to a condition on the ratio of the sphere to neck radii such that (R/h) is less than $(R/h)_{crit}$. When (R/h) is greater than $(R/h)_{crit}$, the potential in the neck region favors oxygen evolution. Oxygen is produced in the neck region, and Pb^{++} ions dissolve from the neck into the electrolyte and are eventually converted to PbO_2 at the sphere. In this manner, when (R/h) is greater than $(R/h)_{crit}$, the lead ions are transferred from the neck to the sphere, and the neck disintegrates, causing conductivity changes in the paste and “shedding.”

The importance of oxygen evolution on battery life and the conductivity changes in the positive plate has caused us to include the oxygen reaction process in our model. The evaluation of oxygen and the subsequent recombination reaction that occurs at the negative electrode are also very important reactions to model for sealed, lead acid batteries. Once we can investigate where the oxygen is evolving, we can investigate where conductivity changes occur in the paste and the consequences on life and charge acceptance. In summary, our approach to solving the performance and life problems of sealed, lead acid batteries is heavily dependent on our models. We use our models to develop a fundamental understanding of the physical processes that limit the performance and life of these batteries. We also use our models to

investigate and develop possible solutions to these problems. In the next section we will present some findings that we obtained with these models.

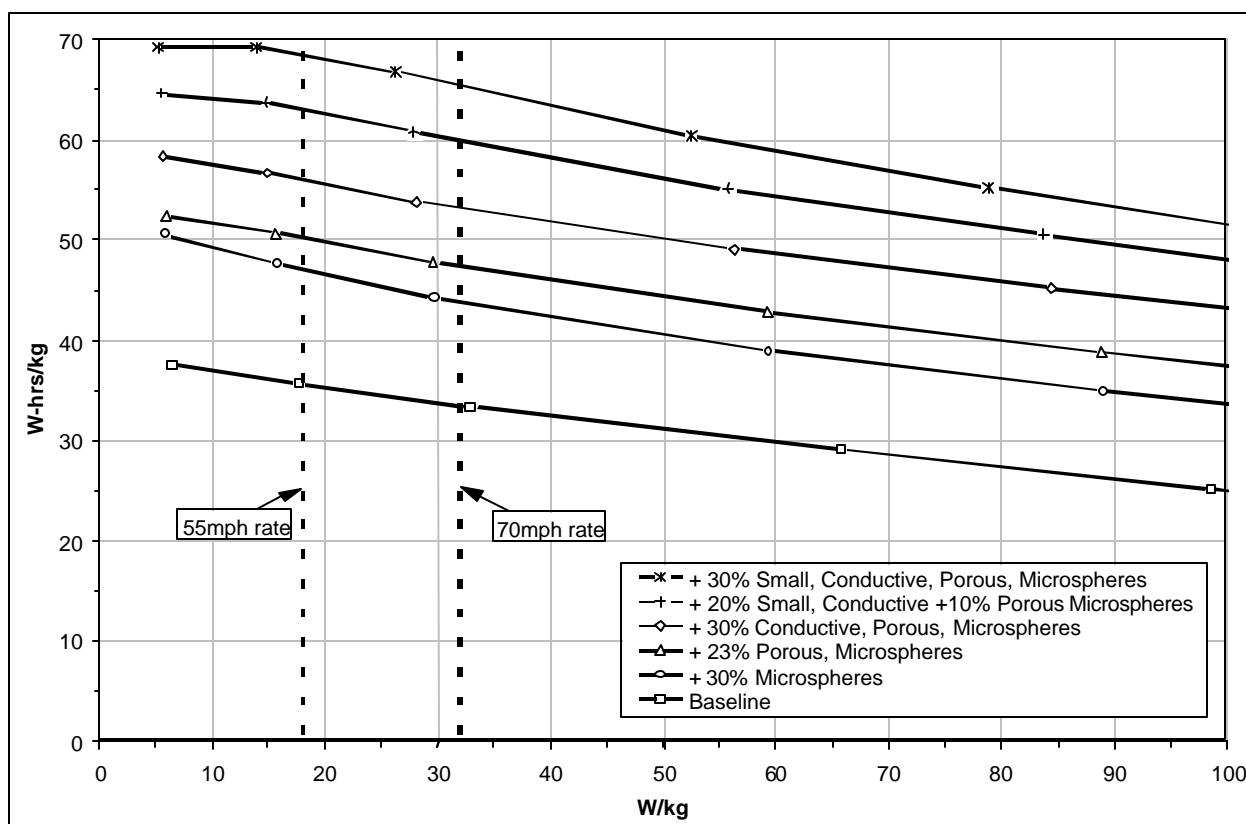


Figure 5. Specific energy (w-hr/kg) versus specific power (W/kg) for all cell models.

FINDINGS; CONCLUSIONS; RECOMMENDATIONS

We have used our models to investigate the use of additives in the positive plate [14]. Figure 4 shows the results of these studies. With the addition of 30 percent by volume of conductive, porous, glass microspheres in the negative and positive active materials, the specific energy of a battery can be increased by 58 percent to an estimated 5060 w-hr/kg. If smaller additive sizes are considered, the specific energy can be increased 95 percent to an estimated 60 to 70 w-hr/kg. By increasing the specific energy of the baseline battery design, the feasibility of using lead acid batteries in electric and hybrid electric vehicles increases. When the discharge times

are examined, the final cell design, discharged at the original one and two-hour rates, would have discharge times nearly double the baseline. This means that for the same battery size and weight, the new cell design would almost double the range of present electric or hybrid electric vehicles. We realize that these projections are based on theoretical models and that much work needs to be performed in order to validate these designs. Some of this future work should be to establish the characteristic size of a node so that the performance of additives can be better modeled.

Battery life can be increased with compression on the positive plate to reduce shedding. Investigators have confirmed that applying approximately 10^5 Pa of mechanical pressure to the face of the positive electrode can dramatically increase the life of deep-cycled, lead acid batteries. It is surprising that such a small amount of mechanical pressure or compression on the positive electrode would have such an extraordinary effect on cycle life. In order to understand the beneficial effect of compression, we should first understand how shedding occurs. Unfortunately, investigators have not agreed on the fundamental causes for shedding.

We have developed a quantitative explanation for how mechanical compression can provide a dramatic improvement, an order of magnitude, in battery life [14]. Table 1 gives the value of the axial pressure (P_A) required to stabilize a sphere of a given radius R . We base our analysis on the concept that a critical ratio exists for the sphere and neck radii $(R/h)_{\text{crypt}}$. The analysis shows that mechanical compression helps to improve life because it causes a broadening of the neck and reduces the (R/h) ratio. Applying axial pressure of about 10^5 Pa to the face of the positive electrode causes the (R/h) ratio of spheres having a radius of $.09 \mu\text{m}$ to be less than $(R/h)_{\text{crit}}$. From BET measurements, the sizes of PbO_2 particles are typically close to this value. The application of this amount of compression, therefore, stabilizes most of the PbO_2 particles in the positive electrode.

Our analysis agrees closely with experimental observations. The magnitude of the mechanical compression we calculate for long battery life is similar to what has been observed—approximately 10^5 Pa. We predict that battery life should increase with an increase in

mechanical compression until most of the particles are stabilized. This prediction also agrees with experimental observations. The close correlation between our analysis and the experimental observations not only helps to explain the beneficial effect of mechanical compression on life, but also helps validate the AOS model. We believe that understanding the process by which oxygen evolution damages the positive plate is a critical step in developing a robust battery and should be included in future work.

Table 1. Compression Analysis Results

Sphere Radius R(mm)	$(R/h)_{crit}$	$P_A (10^5 \text{ Pa})$
1.00	49.7	0.10 ± 0.07
0.50	35.3	0.19 ± 0.13
0.10	16.2	0.91 ± 0.61
0.09	15.4	$1.00 \pm .66$
0.05	11.7	1.76 ± 1.13
0.01	5.2	7.62 ± 5.80

The last finding concerns where oxygen evolution occurs in the positive plate. Figure 6 shows the electrolyte concentrations as a function of position in the cell at different times during the charge. The higher concentrations correspond to the higher charge voltages that occur inside the positive plate. This result is important because several failure mechanisms associated with sealed, lead acid batteries, most notably the premature capacity loss (PCL) mechanism, appears to be related to a loss in active material conductivity. This conductivity loss occurs not at the interface of the grid and active material or at the electrolyte interface, but inside the active material. Again, the explanation that oxygen evolution causes the active material to deteriorate is consistent with this explanation. Future work is needed to quantify where and under what cycling regimes this conductivity loss occurs and to verify the results experimentally.

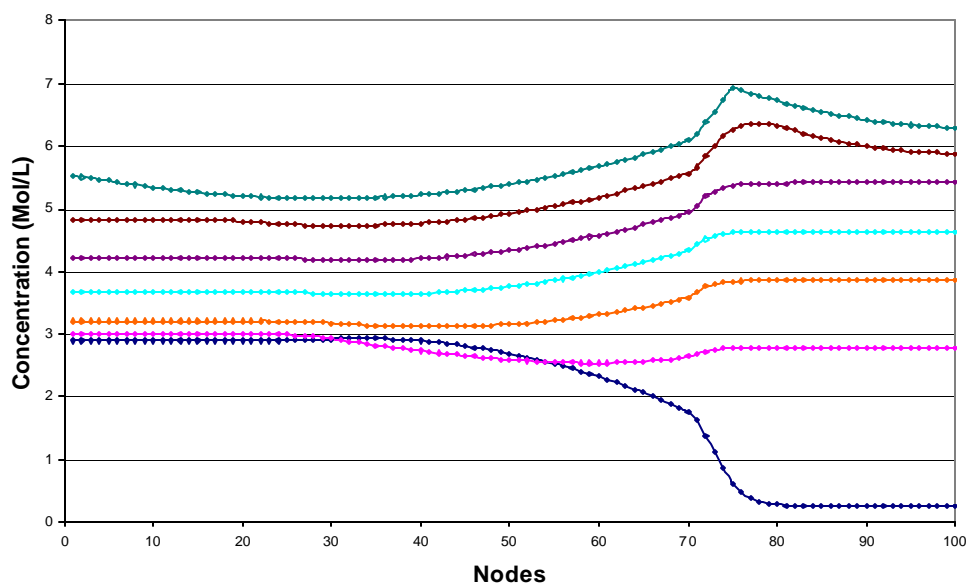


Figure 6. Charge concentration profiles (immediately following discharge).

REFERENCES

1. D. B. Edwards and P. W. Appel, *Journal of Power Sources*, “Conductivity Model for Lead/Acid Battery Electrodes Discharged at Low Rates,” vol. 38, 1992, pp. 281–286.
2. H. Metzendorf, *Journal of Power Sources*, “Capacity Limiting Role of the Electronic Conductivity of the Activity Material in Lead-Acid Batteries During Discharge,” vol. 7, 1982, pp. 281–291.
3. P. W. Appel and D. B. Edwards, *Advanced Performance Materials*, “Understanding and Defeating the Physical Mechanisms Limiting the Capacity of Lead-Acid Batteries,” vol. 3, 1996, pp. 43–45.
4. A. Winsel, E. Voss, and U. Hullmeine, *Journal of Power Sources*, “Aggregate-of-spheres (‘Kugelhauften’) Model of $\text{PbO}_2/\text{PbSO}_4$ Electrode,” vol. 30, 1990, pp. 209–226.
5. U. Hullmeine, A. Winsel and E. Voss, *Journal of Power Sources*, “Effect of Previous Charge/Discharge History on the Capacity of the $\text{PbO}_2/\text{PbSO}_4$ Electrode: The Hysteresis or Memory Effect,” vol. 25, 1989, pp. 27–47.
6. E. Bashtavelova and A. Winsel, *Journal of Power Sources*, “ PbO_2 Active Material as an Electrocrystalline Network.” vol. 46, 1993, pp. 219–230.
7. A. Winsel and E. Bashtavelova, *Journal of Power Sources*, “Agglomerate of Spheres Model: Theoretical Consideration.” vol. 46, 1993, pp. 211–217.
8. E. Bashtavelova and A. Winsel, *Journal of Power Sources*, “Paste Structure and Its Influence on the Agglomerate-of-Spheres Parameters of the PbO_2 Electrode” vol. 63, 1995, pp. 175–183.
9. E. Bashtavelova and A. Winsel, *Journal of Power Sources*, “The PbO_2 Agglomerate-of-Spheres Investigation of Four Grid Materials,” vol. 67, 1997, pp. 93–103.
10. E. Meissner and E. Voss, *Journal of Power Sources*, “Reversible Capacity Decay of Positive Electrodes in Lead/Acid Cells,” vol. 33, 1991, pp. 231–244.
11. E. Meissner and H. Rabenstein, *Journal of Power Sources*, “Reversible Capacity Decay of PbO_2 Electrodes Influence of High-Rate Discharges and Rest Times,” vol. 40, 1992, pp. 157–167.
12. A. Winsel and E. Bashtavelova, *Journal of Power Sources*, “Nanostructure and Agglomerate-of-Spheres Model,” vol. 73, 1998, pp. 242–250.

13. D. B. Edwards and C. Schmitz, *Journal of Power Sources*, “Theoretical Calculations for Using Positive Electrode Compression to Increase Lead-Acid Battery Life,” vol. 85, 2000, pp. 63–71.
14. D. B. Edwards, and T. C. Dayton, *Journal of Power Sources*, “Improving the Performance of a High Power, Lead-Acid Battery with Paste Additives,” vol. 85, 2000, pp. 137–144.